

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
7 June 2001 (07.06.2001)

PCT

(10) International Publication Number  
**WO 01/41152 A2**

- (51) International Patent Classification<sup>7</sup>: **G21C 19/42** (74) Agent: **HARRISON GODDARD FOOTE**; Tower House, Merrion Way, Leeds LS2 8PA (GB).
- (21) International Application Number: **PCT/GB00/04604** (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (22) International Filing Date: 4 December 2000 (04.12.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
9928655.1 3 December 1999 (03.12.1999) GB
- (71) Applicant (*for all designated States except US*): **BRITISH NUCLEAR FUELS PLC** [GB/GB]; Risley, Warrington, Cheshire WA3 6AS (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **HATTER, Justine, Elizabeth** [GB/GB]; British Nuclear Fuels Plc, Risley, Warrington, Cheshire WA3 6AS (GB). **THIED, Robert, Charles** [GB/GB]; British Nuclear Fuels Plc, Sellafield, Seascale, Cumbria CA20 1PG (GB).
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**  
— *Without international search report and to be republished upon receipt of that report.*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



**WO 01/41152 A2**

(54) Title: **ACTINIDE PRODUCTION**

(57) Abstract: The invention provides a process for reducing to metallic form a metal oxide present in spent nuclear fuel, the process comprising cathodically electrolysing the actinide oxide in the presence of a molten salt electrolyte, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of the metal from the cations present in the molten salt. The invention allows for the reduction of the metal oxide to a metallic form by the use of a single electrochemical process, with oxygen being produced as the only by-product.

## ACTINIDE PRODUCTION

### Field of the Invention

This invention relates to methods for the production of metals from oxides present in spent nuclear fuels and is particularly applicable to the production of actinides, for instance uranium, from actinide oxides which are present in irradiated nuclear fuels. Methods of the present invention can be used in the treatment of irradiated fuels for producing actinides in metallic form suitable for use as feeds in subsequent electrorefining processes.

### Background to the Invention

Two processes have been developed for the treatment of irradiated nuclear fuel making use of molten salts. As used herein, the term "molten salts" is intended to cover salts such as lithium chloride which melts at an elevated temperature and also ionic liquids which typically are liquid at room temperature or which melt at a temperature up to about 100°C.

The Dimitrovgrad SSC-RIAR process makes use of chemical oxidants (chlorine and oxygen gases) to react with powdered uranium dioxide fuel to form higher oxidation state compounds such as  $\text{UO}_2\text{Cl}_2$  which are soluble in the molten salt. In an electrochemical cell the uranium compounds are reduced to  $\text{UO}_2$  at the cathode, forming a dendritic deposit. This process has both technical and environmental limitations.

The second process, developed by the Argonne National Laboratory (ANL) is fundamentally an electrorefining technology which uses current flow to oxidise anodic uranium to form uranium ions in the molten salt electrolyte. At the cathode the uranium is reduced and electrodeposited as uranium metal.

The ANL process requires a metal feed. If oxide fuels are to be treated, it is necessary to reduce the uranium oxide (usually  $\text{UO}_2$  pellets) to the metal. This

reduction process is carried out chemically, using lithium metal in a LiCl or LiCl/KCl molten salt at 500 to 600°C. Alternatively, a salt transport process can be used involving a Cu-Mg-Ca alloy and molten CaCl<sub>2</sub> salt. However, in both reduction methods the by-products, Li<sub>2</sub>O and CaO respectively, need to be recovered from the molten salt phase by an electrolysis step. Effectively this means a two stage process.

A disadvantage of the lithium reduction process for producing a metallic feed from an oxide is the production of Li<sub>2</sub>O by-product. This requires recycle to make the process economic, and this is done by an electrolytic recovery of lithium metal. Hence you have a two stage process, a reduction step, followed by a lithium recovery.

### Statements of Invention

According to the present invention there is provided a process for reducing to metallic form a metal oxide present in spent nuclear fuel, the process comprising cathodically electrolysing the oxide in the presence of a molten salt electrolyte, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of the metal from the cations present in the molten salt.

Accordingly, the present invention involves the use of a single electrochemical process to reduce the metal oxide fuel to a metallic form, with oxygen produced as the only by-product. It is important that the potential of the cathode is maintained and controlled so that only oxygen ionisation occurs and not the deposition of the cations (eg Ca ions) in the fused salt.

Typically the oxide comprises an actinide oxide, such as uranium oxide, irradiated uranium oxide or mixed uranium/plutonium oxides.

The oxide may be in any physical form, and this is generally dependent on the particular chemical nature of the spent nuclear fuel and the processing to which the material has previously been subjected. For example, the fuel may comprise a powder, an amorphous mass, or a dense solid agglomerate. In any event, the material

may be treated according to the method of the present invention by connection to an electrical circuit such that it serves as the cathode during electrolysis. Connection to the circuit may be effected by any of the standard means well known to those skilled in the art.

5

Preferably the oxide fuel is in contact with the cathode of an electrochemical cell. The cathode could be in the form of a mesh basket. The molten salt electrolyte may be any suitable molten salt, for instance,  $\text{CaCl}_2$  and  $\text{BaCl}_2$ .

10

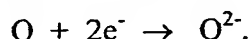
The anode may be any suitable inert anode, such as carbon. In a process of the present invention the oxide fuel may be first treated mechanically to remove its zircaloy cladding before it is added to the electrolytic cell. Alternatively, the zircaloy cladding is first chopped into segments, and these segments are treated by the process of the invention.

15

#### **Detailed description of the Invention**

In order to carry out an embodiment of the present invention, an electrolytic cell is assembled which has a carbon anode and a mesh basket cathode. Irradiated oxide fuel is placed in the mesh basket. The electrolyte consists of a molten salt such as  $\text{CaCl}_2$  or  $\text{BaCl}_2$ . A voltage is applied between the cathode and the anode. At the cathode the reaction involves the diffusion of oxygen atoms to the surface of the molten salt, followed by ionisation according to the reaction:

20



The oxide ions which are produced dissolve in the electrolyte and are transferred to the anode where they are re-oxidised to produce oxygen gas. The potential at the cathode is controlled, via a third reference electrode, to ensure that the reaction occurring at the cathode is oxygen ionisation and not deposition of the cations in the fused salt. Electrolysis at elevated temperatures results in an increased rate of oxygen diffusion, thereby also encouraging ionisation rather than metal deposition.

25  
30

After electrolysis the irradiated fuel is left in the form of a metallic solid at the cathode. This metallic solid, which contains fission products, can be removed and used directly as the feed for an electrorefining process. The remaining components of the cell may be re-used immediately without the need for any cleaning.

5

In an alternative embodiment in accordance with the present invention the electrolytic ionisation of oxygen and the electrorefining processes are carried out in the same cell.

10

It is to be emphasised that the advantage of process of the present invention is that it is effectively a single stage process. It may be used for the treatment of irradiated oxide nuclear fuel, possibly in the form of pellets, and will be applied to fuels such as uranium oxide, and mixed uranium and plutonium fuels known as MOX fuels.

15

Changes in the morphology of spent fuel material comprising uranium oxide have been observed following electrolysis, and these changes are indicative of the electrochemical reduction of the oxide to the metal during the course of the process. Thus, the porous structure associated with the oxide is seen to become much less porous as the metal is formed; this is consistent with the greater mobility of uranium

20

metal, as compared with its oxide.

25

Detailed examination of the products obtained from the reduction of zirconium dioxide has been carried out by means of energy dispersive X-ray analysis (edax) and has allowed for the identification of a metallic solid containing 0.3 wt% oxygen, thereby confirming the success of the process. Similar studies have also been carried out with cerium dioxide, yielding metallic cerium containing 4 wt% oxygen.

## CLAIMS

1. A process for reducing to metallic form a metal oxide present in spent nuclear fuel, the process comprising cathodically electrolysing the oxide in the presence of a molten salt electrolyte, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of the metal from the cations present in the molten salt.
2. A process according to claim 1 wherein the oxide comprises an actinide oxide.
3. A process according to Claim 2 wherein the actinide oxide comprises uranium oxide, irradiated uranium oxide or mixed uranium/plutonium oxide fuel pellets.
4. A process according to Claim 3 wherein the uranium oxide comprises uranium dioxide.
5. A process according to any of the preceding claims wherein the oxide is located in a mesh basket which forms the cathode.
6. A process according to any of the preceding claims wherein the molten salt is  $\text{CaCl}_2$  or  $\text{BaCl}_2$ .
7. A process according to any of the preceding claims wherein the anode is a carbon anode.
8. A process according to any of the preceding claims wherein the fuel is treated together with its cladding.

9. A process according to Claim 8 wherein the cladding is removed from the fuel prior to electrolytic treatment.

10. A process according to any of the preceding claims wherein the metal  
5 resulting from the process is used as the feed for an electrorefining process.

11. A process according to Claim 10 wherein the electrorefining process is carried out in the same electrolytic cell as the electrolytic reduction process.

10 12. A process according to Claim 1 and substantially as herein described.

15

20

25

30

**THIS PAGE BLANK (USPTO)**



(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
7 June 2001 (07.06.2001)

PCT

(10) International Publication Number  
**WO 01/41152 A3**

(51) International Patent Classification<sup>7</sup>: **G21C 19/48,**  
C25C 3/34

(21) International Application Number: PCT/GB00/04604

(22) International Filing Date: 4 December 2000 (04.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
9928655.1 3 December 1999 (03.12.1999) GB

(71) Applicant (for all designated States except US): **BRITISH NUCLEAR FUELS PLC** [GB/GB]; Risley, Warrington, Cheshire WA3 6AS (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HATTER, Justine,** Elizabeth [GB/GB]; British Nuclear Fuels Plc, Risley, Warrington, Cheshire WA3 6AS (GB). **THIED, Robert,** Charles [GB/GB]; British Nuclear Fuels Plc, Sellafield, Seascale, Cumbria CA20 1PG (GB).

(74) Agent: **HARRISON GODDARD FOOTE;** Belgrave Hall, Belgrave Street, Leeds LS2 8DD (GB).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:  
— with international search report

(88) Date of publication of the international search report:  
21 March 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **ACTINIDE PRODUCTION**

(57) Abstract: The invention provides a process for reducing to metallic form a metal oxide present in spent nuclear fuel, the process comprising cathodically electrolysing the actinide oxide in the presence of a molten salt electrolyte, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of the metal from the cations present in the molten salt. The invention allows for the reduction of the metal oxide to a metallic form by the use of a single electrochemical process, with oxygen being produced as the only by-product.

WO 01/41152 A3

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/04604

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 G21C19/48 C25C3/34

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 G21C C25C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US H857 H (P.A.HAAS) 4 December 1990 (1990-12-04) the whole document	1
A	US 4 880 506 A (ACKERMAN JOHN P ET AL) 14 November 1989 (1989-11-14) the whole document	1
A	US 5 650 053 A (GAY EDDIE C ET AL) 22 July 1997 (1997-07-22) the whole document	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

**\* Special categories of cited documents :**

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*A\* document member of the same patent family

Date of the actual completion of the international search

5 September 2001

Date of mailing of the international search report

19/09/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Brothier, J-A

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Publication No

PCT/GB 00/04604

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US H857	H	04-12-1990	NONE	
US 4880506	A	14-11-1989	CA 1326839 A DE 3837572 A GB 2212171 A,B JP 1237497 A JP 2641533 B	08-02-1994 18-05-1989 19-07-1989 21-09-1989 13-08-1997
US 5650053	A	22-07-1997	NONE	

**THIS PAGE BLANK (USPTO)**